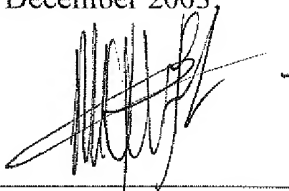


## **Certificate of Translation**

I, Nadège M. LAGNEAU, Ph.D., declare that I am suitably proficient in both English and French to translate; and hereby certify that, to the best of my knowledge, ability and belief, the attached document is an accurate and complete translation of French Patent Application N° FR 03/15582 filed in the French Patent Office on 30 December 2003.

**Dated:** September 1, 2009



---

Nadège M. LAGNEAU, Ph.D.

NOVAGRAAF IP  
122 Avenue Edouard Vaillant  
92593 Levallois-Perret CEDEX  
FRANCE

## Method for dissolving carbon nanotubes and uses thereof

The subject of the invention is a method of dissolving carbon nanotubes and its applications, especially for the manufacture of composites and the purification of nanotubes.

To obtain nanotubes in the form of solutions is of great benefit for their industrial applications, in particular for forming them for a given use. Such solutions can be readily used to form nanotube films or to produce, by impregnation, composites containing nanotubes. They also open the way to purifying nanotubes.

At the present time, carbon nanotubes are most generally dispersed by the addition of surfactants or polymeric dispersants, and exposed to ultrasound, or by functionalization.

However, these methods have the drawback, respectively, of damaging the nanotubes and of denaturing them.

In the first method, the surfactants cannot easily be desorbed from the surface of the nanotubes, which prevents essential intertube contacts for the exploitation, in particular, of their electronic properties. These solutions must in general be subjected to high doses of ultrasound in order to dissolve the nanotubes, which results in the nanotubes being chopped into shorter, and therefore less anisotropic, fragments, thereby diminishing one fundamental and specific characteristic of carbon nanotubes. As a result, the properties of the nanotubes are impaired. Finally, the systems obtained are metastable from a thermodynamic standpoint and have a tendency to re-aggregate over time.

The second method leads to the formation of functional groups on the surface of the nanotubes and on their ends, hence denaturation which, here again, precludes complete exploitation of the exceptional mechanical, electrical and optical properties of nanotubes.

The work by the inventors was aimed at seeking a method for dissolving nanotubes without using surfactants or polymeric dispersants and ultrasound, and without acid treatments. Thus, it has turned out that these objectives can be achieved by reducing, for example chemically or electrochemically, nanotube specimens.

The object of the invention is therefore to provide a method of dissolving nanotubes that allows their integrity, and hence their properties, to be preserved.

According to the invention, the method of dissolving carbon nanotubes is characterized in that it comprises the reduction of nanotubes, which results in negatively charged nanotubes with positive counterions.

According to a preferred arrangement, the counterions are alkali metal cations.

The invention also relates to a method of dissolving carbon nanotubes that is characterized in that it includes the addition, under anaerobic conditions, to the nanotubes of a salt of formula:



in which:

-  $A^+$  represents a cation of an alkali metal ion, such as lithium or sodium; and

-  $B^-$  represents an anion of a polyaromatic compound, so as to electrically charge the nanotubes, the anion of the polyaromatic compound being a reducing agent for these nanotubes.

The nanotubes are separated from the medium by filtration and dried. In a second step a polar solvent is added, which results in a dissolved phase with the nanotubes and an undissolved phase. The nanotube solutions are then separated, for example by centrifugation of the solid residue.

It should be noted that this solution treatment, which, as emphasized above, increases the technological options of preparing carbon nanotube devices, results in no denaturation of the nanotubes.

In particular, it will be seen that it is sufficient to place fewer nanotubes in a matrix in order to obtain equivalent or superior properties (e.g., in transparent films) than those obtained with the current techniques, the length of the nanotubes having been maintained.

Advantageously, the polyaromatic compound is chosen from naphthalene, benzophenone, fluorenone, anthraquinone and benzoquinone.

Suitable polar organic solvents for implementing the invention comprise sulfolane, dimethyl sulfoxide, dimethylformamide, N-methylpyrrolidone and N-methylformamide.

According to one arrangement of the invention, the nanotubes contain boron as a substitute for carbon.

In one embodiment of the invention, the nanotubes used are single-walled nanotubes.

In another embodiment, the nanotubes are multi-walled nanotubes.

Depending on the envisaged applications, the nanotubes used are empty nanotubes, or else they contain molecules, for example photosensitive molecules or fullerenes, salts, such as alkali metal halides, or else threads of metal elements.

The method of dissolving carbon nanotubes may further include, according to the invention, a step of purifying the nanotubes.

The method may also include a step of functionalizing the surface or the ends of the nanotubes.

Advantageously, the solutions obtained according to the invention are used directly for impregnating polymers, for manufacturing antistatic plastics, or for mechanical reinforcement, or for electromagnetic shielding, or else they are deposited on substrates in order to form thin, optionally oriented, films with electrooptic properties.

Starting from these solutions, it is possible to purify the nanotubes (for example by crystallization/precipitation, chromatography, electrophoresis, etc.), to obtain nanotube mesophases (liquid crystals), bucky papers and generally to carry out forming operations

resulting in any type of device that exploits the greatly beneficial mechanical, electrical and optical properties of carbon nanotubes.

In particular, these solutions lead to conducting transparent coatings, either by mixing with a polymer soluble in organic solvents, or by mixing with a monomer followed by subsequent polymerization.

Other features and advantages of the invention are given in the examples that follow, with reference to the single figure, which shows an image of the solid sample obtained from a solution of carbon nanotubes in DMSO, taken by a scanning electron microscopy.

#### Example 1: Synthesis of a Carbon Nanotube Lithium Salt

The procedure was carried out under a controlled atmosphere (for example under argon). This salt was obtained by reaction of a carbon nanotube suspension in THF in which a naphthalene salt, namely  $\text{Naph}^-\text{Li}^+$  (Naph=naphthalene), was dissolved using a method modified from P. Petit et al., Chemical Physics Letters, 1999, 305, 370-374 and E. Jouguelet et al., Chemical Physics Letters, 2000, 318, 561-564.

In particular, the  $\text{Naph}^-\text{Li}^+$  salt was prepared by reacting naphthalene with an excess of lithium in THF until a very dark green, almost black, color developed.

This  $\text{Naph}^-\text{Li}^+$  solution was then added to raw carbon nanotubes obtained by the electric arc method and left, with stirring, for a few hours. The nanotubes were then filtered and rinsed with THF until all coloration of the latter on contact with the nanotubes disappeared. They were then vacuum-dried at room temperature.

By way of illustration, an example of a synthesis carried out on a laboratory scale is reported: all the handling operations were carried out in a glove box in a dry argon atmosphere ( $\text{O}_2$  content <5 ppm;  $\text{H}_2\text{O}$  content <1 ppm).

320 milligrams of naphthalene were placed in a 250 cc flask to which 30 milligrams of lithium in the form of small pieces of shiny surface (peeled with a scalpel just before use) and then about 100 cc of THF were added. The flask was heated to reflux until the solution turned a very dark green, and left at reflux for a few hours. This solution was then poured over a filter, in order to avoid an excess of solid lithium, onto 180 milligrams of raw nanotubes (synthesized by the electric arc method). The whole assembly was left with stirring at room temperature for four hours. Alternatively, the reduction in  $\text{Naph}^-\text{Li}^+$  concentration can be monitored by UV/visible spectroscopy. This solution was filtered over a membrane of the Millipore® type (0.45 micron pores). The solid was rinsed several times with THF (distilled over a lithium/naphthalene mixture) until the THF remained colorless after passing through the filter. The solid was then vacuum-dried at room temperature. It exhibited good storage stability over at least several months, in a controlled atmosphere.

In another experiment, the procedure was as indicated above but 390 mg of naphthalene, 120 mg of sodium metal and 220 mg of raw nanotubes were used, then all this was stirred for about 15 h.

Preparation of the solutions: Various polar organic solvents (sulfolane, dimethyl sulfoxide, dimethyl formamide, N-methylpyrrolidone, etc.) were added to the doped nanotubes. After a

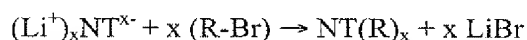
few minutes to a few hours, a more or less dark solution was obtained, the darkness depending on the solubility of the nanotubes in the solvent.

Regeneration of the neutral character of the nanotubes: In order for the nanotubes to be able to be easily handled in the open air for applications not requiring the nanotubes to be electrically charged, their neutral state was restored either by exposing the solution to air, or, in order to speed up the process, by adding water or toluene.

In all these cases, the nanotubes re-aggregated and it was then sufficient to filter the solution in order to recover the soluble fraction.

Example of solubilization: 19.5 mg of sodium-doped nanotubes in 2 cc of DMSO were stirred for about 14 h under a controlled atmosphere at room temperature. The resulting solution was centrifuged at 5000 rpm for 1 h, and was then decanted. A homogeneous solution of nanotubes was obtained, that is to say one not containing aggregates visible with an optical microscope (x1000 magnification). A solubility of 4.9 mg of sodium-doped nanotubes per gram of DMSO was obtained.

Example of functionalization: An organic group R was attached to a nanotube by carrying out the reaction:



where NT denotes a nanotube, and x denotes an integer corresponding to the stoichiometry.

## CLAIMS

1/ A method of dissolving carbon nanotubes, characterized in that it comprises the reduction of nanotubes, which results in negatively charged nanotubes with positive counterions.

2/ The method as claimed in claim 1, characterized in that the counterions are alkali metal cations.

3/ The method as claimed in claim 1 or 2, characterized in that it includes the addition, under anaerobic conditions, to the nanotubes of a salt of formula:



in which:

$A^+$  represents a cation of an alkali metal ion, such as lithium or sodium; and

$B^-$  represents an anion of a polyaromatic compound,

so as to electrically charge the nanotubes.

4/ The method as claimed in claim 3, characterized in that the aromatic compound is chosen from naphthalene, benzophenone, fluorenone, anthraquinone and benzoquinone.

5/ The method according to any one of claims 1 to 4, characterized in that the polar organic solvents are chosen from sulfolane, dimethyl sulfoxide, dimethylformamide, N-methylpyrrolidone and N-methylformamide.

6/ The method according to any one of the preceding claims, characterized in that the nanotubes contain boron as a substitute for carbon.

7/ The method according to any one of the preceding claims, characterized in that the nanotubes used are single-walled nanotubes.

8/ The method according to any one of claims 1 to 7, characterized in that the nanotubes used are multi-walled nanotubes.

9/ The method according to claim 7 or 8, characterized in that the nanotubes used are empty nanotubes.

10/ The method according to claim 7 or 8, characterized in that the nanotubes used contain molecules, for example photosensitive molecules or fullerenes, salts, such as alkali metal halides, or else threads of metal elements.

11/ The method according to any one of the preceding claims, characterized in that it further includes a step of purifying the nanotubes.

12/ The method according to any one of the preceding claims, characterized in that it further includes a step of functionalizing the surface or the ends of the nanotubes.

13/ The application of the method according to any one of the preceding claims to the preparation of composites having improved properties or of oriented or unoriented thin films of carbon nanotubes, or of composite films.

14/ The application as claimed in claim 13, as mechanical reinforcements, antistatic materials and materials for electromagnetic shielding.

15/ The application as claimed in claim 13, as electrically conducting transparent coatings.

SINGLE FIGURE

